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PHASE RELATIONS IN SUBSOLIDUS AREA OF $ZnO–V_2O_5–Fe_2O_3$ SYSTEM

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Abstract

Phase equilibria in subsolidus area in the $ZnO–V_2O_5–Fe_2O_3$ system have been investigated over the whole concentration range of the oxides. The components of this system form two compounds: $Zn_2FeV_3O_{11}$ and $Zn_3Fe_4(VO_4)_6$. A solidus area projection onto the component concentration triangle plane of the $ZnO–V_2O_5–Fe_2O_3$ system has been constructed using DTA and XRD methods. 11 subsidiary subsystems can be distinguished in this system. Melting temperatures of mixtures of solid phases coexisting at equilibrium in each of subsidiary subsystems were determined.

Keywords: DTA, Fe_2O_3, phase relations, V_2O_5, ZnO, XRD

Introduction

Vanadates(V) and molybdates(VI) of divalent metals exhibiting the presence of isolated MO_4 tetrahedra in their structure display a good selectivity and high activity as catalysts of oxidative dehydrogenation of light alkanes [1–5]. Such properties are also characteristic of the compound $Mg_{2.5}VMoO_8$ known for not long [6]. Among phases recently obtained there are some with a structure related with $Mg_{2.5}VMoO_8$, i.e. $Mg_2FeV_3O_{11}$ [7] and $Co_2FeV_3O_{11}$ [8]. These new compounds are formed in the systems $MgO–V_2O_5–Fe_2O_3$ and $CoO–V_2O_5–Fe_2O_3$, respectively.

The analogous $ZnO–V_2O_5–Fe_2O_3$ system had not been a subject of any thorough works before our investigations. Recent papers on the $ZnO–V_2O_5–Fe_2O_3$ system have shown that its components form two new compounds, $Zn_2FeV_3O_{11}$ [7, 9] and $Zn_3Fe_4(VO_4)_6$ [10]. Both compounds contain isolated VO_4 tetrahedra in their structures [7, 11].

In our subsequent works on the system $ZnO–V_2O_5–Fe_2O_3$, diagrams of phase equilibria of three non-isothermal intersections contained in the subsolidus area have been worked out (Fig. 1). These intersections lie on quasi-binary lines linking ZnV_2O_6 with $ZnFe_2O_4$ [12] or $FeVO_4$ with $Zn_3(VO_4)_2$ [13] and with $Zn_2V_2O_7$ [14]. Only the system $ZnV_2O_6–ZnFe_2O_4$ is a real binary system in the subsolidus area. In this system, a compound $Zn_2FeV_3O_{11}$ [9] is formed at a molar ratio of $ZnV_2O_6/ZnFe_2O_4$ equal to 3:1. In the

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$FeVO_4$–$Zn_3(VO_4)_2$ system, another new compound – $Zn_3Fe_4(VO_4)_6$ – is formed at a molar ratio of the components equal to 4:1. This system is actually binary only up to 20 mol% $Zn_3(VO_4)_2$. In the remaining component concentration range, there is an intersection of the ternary system ZnO–V_2O_5–Fe_2O_3, crossing its three subsidiary subsystems $ZnFe_2O_4$–$Zn_3Fe_4(VO_4)_6$–$Zn_2FeV_3O_{11}$, $Zn_2V_2O_7$–$Zn_2FeV_3O_{11}$–$ZnFe_2O_4$ and $Zn_2V_2O_7$–$Zn_4V_2O_9$–$ZnFe_2O_4$ [13]. In the third system $FeVO_4$–$Zn_2V_2O_7$ in the components concentration range up to 50 mol% $FeVO_4$, there exist two solid phases at equilibrium, $Zn_2V_2O_7$ and $Zn_2FeV_3O_{11}$, and only in this concentration range the system is actually binary. In the remaining range, the system is an intersection of the ZnO–V_2O_5–Fe_2O_3 system, crossing three subsidiary subsystems $Zn_2FeV_3O_{11}$–$Zn_3Fe_4(VO_4)_6$–V_2O_5, $Zn_3Fe_4(VO_4)_6$–V_2O_5–$Fe_2V_4O_{13}$ and $Zn_3Fe_4(VO_4)_6$–$Fe_2V_4O_{13}$–$FeVO_4$ [14].

Diagrams of phase equilibria of these intersections and literature information have supplied enough data to enable a preliminary dividing of the subsolidus area of the ZnO–V_2O_5–Fe_2O_3 system into subsidiary subsystems (Fig. 1).

The aim of the presented work was to verify the conclusions drawn on the base of the described state of investigations, as well as working out a phase diagram of the subsolidus area of the system ZnO–V_2O_5–Fe_2O_3.

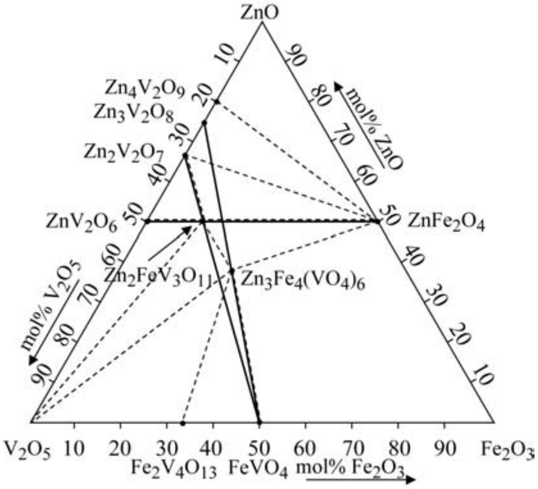

Fig. 1 Investigated non-isothermal intersections of ZnO–V_2O_5–Fe_2O_3 system (solid lines) and preliminary dividing of subsolidus area into subsidiary subsystems (dashed lines)

Experimental

The reacting substances used in the research were: Fe_2O_3 (p.a. product of POCh Gliwice, Poland), V_2O_5 (p.a. product of Riedel-de Haën, Germany), ZnO (p.a. Ubichem, England) and several ones obtained as a result of solid-state reactions: $Zn_3(VO_4)_2$, $ZnFe_2O_4$, ZnV_2O_6, $Zn_2V_2O_7$, $FeVO_4$, $Zn_2FeV_3O_{11}$ and $Zn_3Fe_4(VO_4)_6$.

For the investigations, 13 samples were prepared – comprising mixtures of the phases considered on the base of earlier research to co-exist at equilibrium in given areas. These mixtures were heated, after shaping them into pellets, for 24 h at temperatures lower by 40ºC than the temperature of the corresponding solidus line and then they were rapidly cooled down to ambient temperature, ground and subjected to investigation by XRD and DTA method. Results of XRD and DTA investigations allow a determination of composition of samples and an establishing of their melting temperatures [15–17].

The composition of the samples was established on the ground of their powder diffraction patterns obtained by means of an X-ray diffractometer DRON-3 (Bourevestnik, Sankt Petersbug, Russia). The radiation source was cobalt tube (CoK_α) with Fe filter. The identification of the phases was performed on the base of the X-ray characteristics contained in the PDF cards [18] and the data reported in [9, 10, 19].

The DTA investigation was conducted by means of a Paulik–Paulik–Erdey derivatograph (MOM, Hungary). The measurements were performed in the atmosphere of air in the temperature range 20–1000ºC. Portions weighing as much as 500 mg were heated in quartz crucibles at a heating rate of 10°C min^{-1}. The accuracy of reading the temperatures of thermal effects, as determined on the base of repetitions, amounted to ±5ºC. The reference substance was α-Al_2O_3.

Results and discussion

13 verifying samples were prepared. They comprised mixtures of phases that ought to be existing at equilibrium in accordance with deduced preliminary dividing of the subsolidus area of the ZnO–V_2O_5–Fe_2O_3 system into subsidiary subsystems (Fig. 1).

Table 1 lists the compositions of these samples in terms of the ZnO–V_2O_5–Fe_2O_3 system's components. Results of XRD investigations showed that the compositions of these samples did not change despite their prolonged heating at temperatures close to their melting temperatures. The type of solid phases remaining at equilibrium with one another are given in Table 1, column 5. The obtained results have thus confirmed the conclusions implied by the investigations performed already and dealing with the phase relations in the binary systems being intersections of the system ZnO–V_2O_5–Fe_2O_3.

A phase diagram of this system in the subsolidus area was worked out on the base of the results of research on the phase relations in the intersections ZnV_2O_6–$ZnFe_2O_4$, $FeVO_4$–$Zn_3(VO_4)_2$ and $FeVO_4$–$Zn_2V_2O_7$, the results of the verifying investigations (Table 1) and the literature data. Fragments of DTA curves of mixtures of phases co-existing in given areas are presented in Fig. 2. Onset temperatures of first endothermic effects (being not an effect of a polymorph transition) read from these curves were assumed as temperatures solidus of respective subsidiary subsystems. Figure 3 presents a projection of the solidus surface on the plane of the component concentration triangle of this system.

Table 1 Composition of using samples and type of solid phases remaining at equilibrium

No.	Composition of using samples in terms of components of ZnO–V_2O_5–Fe_2O_3 system/mol%			Phases remaining at equilibrium
	ZnO	V_2O_5	Fe_2O_3	
1	6.82	54.55	38.63	$FeVO_4$, $Fe_2V_4O_{13}$, $Zn_3Fe_4(VO_4)_6$
2	20.00	55.00	25.00	$Zn_3Fe_4(VO_4)_6$, V_2O_5, $Fe_2V_4O_{13}$
3	26.92	61.54	11.54	$Zn_2FeV_3O_{11}$, V_2O_5, $Zn_3Fe_4(VO_4)_6$
4	33.34	33.33	33.33	$Zn_3Fe_4(VO_4)_6$, Fe_2O_3
5	36.36	54.54	9.10	$Zn_2FeV_3O_{11}$, V_2O_5
6	40.00	10.00	50.00	$Zn_3Fe_4(VO_4)_6$, $ZnFe_2O_4$, Fe_2O_3
7	40.00	55.00	5.00	V_2O_5, ZnV_2O_6, $Zn_2FeV_3O_{11}$
8	47.00	37.50	15.50	$Zn_2FeV_3O_{11}$, $Zn_3Fe_4(VO_4)_6$
9	16.67	33.33	50.00	$FeVO_4$, $Zn_3Fe_4(VO_4)_6$, Fe_2O_3
10	55.00	40.00	5.00	ZnV_2O_6, $Zn_2V_2O_7$, $Zn_2FeV_3O_{11}$
11	64.28	28.57	7.15	$Zn_2V_2O_7$, $ZnFe_2O_4$
12	71.43	14.28	14.29	$Zn_4V_2O_9$, $ZnFe_2O_4$
13	80.00	10.00	10.00	ZnO, $Zn_4V_2O_9$, $ZnFe_2O_4$

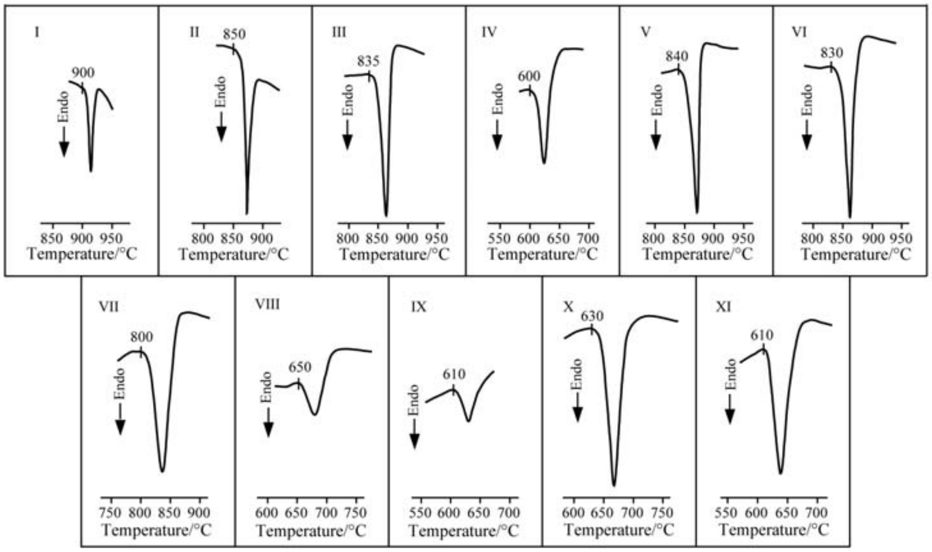

Fig. 2 Fragments of DTA curves on the base of which melting temperatures of respective subsidiary subsystems were determined (Roman numerals denote the numbers of corresponding subsidiary subsystems)

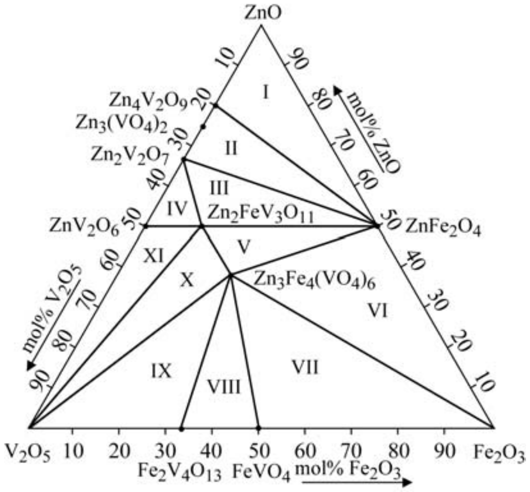

Fig. 3 Phase diagram of subsolidus area of ZnO–V_2O_5–Fe_2O_3 system

The phase diagram allows a distinguishing of 11 subsidiary subsystems inside the ZnO–V_2O_5–Fe_2O_3 system, in which three solid phases co-exist at equilibrium in every case. These are the following subsystems:

I	$Zn_4V_2O_9$–ZnO–$ZnFe_2O_4$	onset temperature of melting=	900±5°C
II	$Zn_4V_2O_9$– $ZnFe_2O_4$–$Zn_2V_2O_7$	onset temperature of melting=	850±5°C
III	$Zn_2V_2O_7$–$ZnFe_2O_4$– $Zn_2FeV_3O_{11}$	onset temperature of melting=	835±5°C
IV	$Zn_2V_2O_7$–$Zn_2FeV_3O_{11}$–ZnV_2O_6	onset temperature of melting=	600±5°C
V	$Zn_2FeV_3O_{11}$–$ZnFe_2O_4$–$Zn_3Fe_4(VO_4)_6$	onset temperature of melting=	820±5°C
VI	$Zn_3Fe_4(VO_4)_6$–$ZnFe_2O_4$–Fe_2O_3	onset temperature of melting=	830±5°C
VII	$FeVO_4$–$Zn_3Fe_4(VO_4)_6$–Fe_2O_3	onset temperature of melting=	800±5°C
VIII	$Fe_2V_4O_{13}$–$Zn_3Fe_4(VO_4)_6$–$FeVO_4$	onset temperature of melting=	650±5°C
IX	$Fe_2V_4O_{13}$–V_2O_5–$Zn_3Fe_4(VO_4)_6$	onset temperature of melting=	610±5°C
X	V_2O_5–$Zn_2FeV_3O_{11}$–$Zn_3Fe_4(VO_4)_6$	onset temperature of melting=	630±5°C
XI	V_2O_5–ZnV_2O_6–$Zn_2FeV_3O_{11}$	onset temperature of melting=	610±5°C

In none of the listed subsidiary subsystems there exists a component $Zn_3(VO_4)_2$, which is due to its decomposition into two solid phases, $Zn_4V_2O_9$ and $Zn_2V_2O_7$, occurring at 800°C [20].

Conclusions

- It has been shown that two compounds, $Zn_2FeV_3O_{11}$ and $Zn_3Fe_4(VO_4)_6$, are formed in the ZnO–V_2O_5–Fe_2O_3 system, involving all three oxides.
- 11 subsidiary subsystems can be distinguished in the investigated system, in which three solid phases co-exist at equilibium in every case.

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